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A new technique has been developed for growing high quality, ultrathin oxide layers on metal films, suitable for use as tunneling barriers in Josephson junction devices. The oxides are produced with an argon-oxygen ion beam, and the rate of growth is determined by the competition between oxidation and sputtering by the ions. The oxidation technique has been applied to the fabrication of high current density submicron niobium-lead alloy Josephson junctions. High quality junctions have been produced with critical current densities exceeding $10^5$ amp/cm$^2$ and having low leakage currents at voltages below

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the energy gap. An edge geometry has been developed, allowing in-line junctions to be formed on the ion mill-patterned edge of Nb film. In this way, junction width is controlled by the Nb film thickness.

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FABRICATION OF JOSEPHSON TUNNEL JUNCTIONS
BY REACTIVE ION MILLING

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A new technique has been developed for growing high
quality, ultrathin oxide layers on metal films, suitable for
use as tunneling barriers in Josephson junction devices.
The oxides are produced with an argon-oxygen ion beam, and
the rate of growth is determined by the competition between
oxidation and sputtering by the ions.  The oxidation tech-
nique has been applied to the fabrication of high current
density submicron niobium-lead alloy Josephson junctions.
High quality junctions have been produced with critical
current densities exceeding $10^5$ amp/cm$^2$ and having low
leakage currents at voltages below the energy gap.  An
edge geometry has been developed, allowing in-line junctions
to be formed on the ion mill-patterned edge of Nb film.  In
this way, junction width is controlled by the Nb film thick-
ness.

*100,000 amp/sq cm*

## I.  INTRODUCTION

Reactive gases have long been used in sputter deposition and
etching (1), and the technique of reactive sputtering has been ex-
tended to include reactive ion etching, in which the chemical compo-
nent of the etching process is emphasized (2).  Although these
techniques are primarily associated with attempts to enhance etching
rates and achieve anisotropic etching for patterning purposes, it is
basically a reactive sputtering technique which was introduced by
Greiner (3) to fabricate Josephson tunneling barriers on supercon-
ducting films.

Ion milling is an extension of the technique of sputter etching
and, recently, work has been reported on reactive ion milling (4-9),
in which reactive gases are either added to the ion source (4-7) or
introduced in the region of the substrate (8,9).  Significant en-
hancement of etching has been reported in organic materials (4) and
SiO$_2$ (5,6,8,9), but results in Si (5,8,9) and metals (7,8) have not
been as striking, at least with low accelerator voltages.  As with
reactive sputtering, reactive ion milling can be used to produce
chemical changes on a substrate surface.  We have applied this prin-
ciple to devise a new technique for growing thin oxide films, primari-
ly for Josephson junction applications.

In fabricating Josephson tunnel junctions it is desirable to use
a hard material, such as niobium, at least for the base electrode in

order to provide mechanical stability and thermal cyclability. In fact, niobium has become the superconductor of choice for many applications. In most cases, this means that the tunneling barrier will be niobium oxide. Here problems are encountered due to the existence of numerous oxide phases. In addition to $Nb_2O_5$, which is the desired tunneling barrier, $NbO_2$, $NbO$, and various suboxides can form, as can niobium-oxygen mixtures. The presence of these phases can seriously impair junction performance. For example, there is some evidence (10) that the interface between $Nb$ and $Nb_2O_5$ in thermally grown oxide films consists of $NbO$ and $NbO_2$, and poor junction quality has been attributed to such layers. Tunnel junctions have been successfully fabricated on $Nb$ using thermal (11) and dc glow discharge oxidation (12,13), however the rf plasma oxidation technique (3) results in the highest current densities (14), an important consideration in high performance junctions.

The rf plasma oxidation method relies upon the competition between oxidation and sputter etching to determine the growth rate of the oxide film. With lead, a steady state thickness is eventually reached, after which the oxide thickness remains constant with time. With niobium, however, good junction quality depends upon oxidizing in a regime in which sputter etching is insignificant (15). Attempts to perform the oxidation with sputter etching present results in the presence of undesirable niobium oxides and poor junction quality (14, 16). In addition, care must be taken as to what materials are present in the vacuum system, since extensive scattering of sputtered material occurs at the gas pressures used.

Ion milling offers a number of advantages over sputter etching. Among them are confinement of the discharge to a region away from the substrates, control of substrate bombardment, and low operating pressures. In an unneutralized argon-oxygen ion beam, only $Ar^+$, $O^+$, and $O_2^+$ are likely to be present, while negative ions are not present in the beam (neutral species are, of course, present in the system). This is in contrast to the rf plasma technique, in which negative ions are thought to be important in the oxidation process (3,15). The mean free path of species in the gas is at least 25 times longer at typical ion milling pressures ($2 \times 10^{-4}$ torr), so that impurity problems resulting from scattering of sputtered material are reduced greatly. No special cleaning or other preparation of surfaces, such as the substrate holder, is necessary, and high quality tunnel junctions can be fabricated in an ordinary vacuum system.

## II. FABRICATION

We have used an argon-oxygen beam produced by a commercial Kaufmann type ion beam source (17) as a means of growing niobium oxide films. Fabrication proceeds as follows: A niobium film is deposited on a sapphire or glass substrate by rf bias sputtering. A

typical film has a resistance ratio ($R_{300K}/R_{10K}$) exceeding 3 and a
transition temperature of 9.2K. The niobium film is patterned by
chemical etching and ion milling using a photoresist mask. The
counterelectrode pattern is then defined by photolithography. The
film is placed in the ion beam system (the vacuum system is a diffu-
sion-pumped bell jar system with a liquid nitrogen trap. Typical
base pressure is around $10^{-6}$ torr) and cleaned in a low current
density (.15 mA/cm$^2$) neutralized argon beam (acceleration voltage:
600V, Ar pressure: $2 \times 10^{-4}$ torr in chamber). Oxygen ($1 \times 10^{-5}$ -
$1 \times 10^{-4}$ torr) is then admitted to the ion source, and oxidation is
carried out at a reduced current density (5 - 150 µA/cm$^2$) in an un-
neutralized beam for a time of less than 1 minute. The counter-
electrode, ε-phase Pb-Bi (18,19) is then immediately deposited. The
substrate table is cooled by liquid nitrogen throughout the entire
procedure. The counterelectrode is patterned by liftoff. The com-
pleted junction is protected by a layer of Kodak photoresist.

Junction areas can easily be reduced by at least a factor of 10
by using an edge geometry, in which the thickness of a thin film
defines one of the junction dimensions (20-22). In our technique,
edges are defined by coating a portion of the Nb counterelectrode
with a film of Al$_2$O$_3$, which is ion beam deposited in an argon-oxygen
atmosphere. Ion milling is then used to form the edge (Fig. 1). The
counterelectrode overlaps the Nb, but can only make contact at the
edge, since the Nb top surface is protected by the Al$_2$O$_3$ film (Fig. 2).
The resulting devices had areas of 1-2µ x .1-.2µ. The characteristics
of these junctions were essentially identical to those of the simple
overlap junctions described above, although the thickness of oxide
formed on an edge was found to be less than that formed on top of a
film, for a given set of oxidation parameters.


III. OXIDATION

The ion beam oxidation method, like the rf plasma technique,
involves, in principle, simultaneous sputter etching and oxide
growth. However, the etching rate for Nb in the ion beam system with
a beam current of .15 mA/cm$^2$ is approximately .12 Å/sec. The etch
rate of Nb$_2$O$_5$ is significantly lower than that of Nb. For ion beam
oxidation, the current density is usually kept between 5 and 30 µA/cm$^2$
for best results. A typical oxide barrier (thickness approximately
20 Å) is grown in less than a minute. Thus sputter etching of the
oxide is thought to be insignificant.

Preliminary experiments have been performed in which lower oxygen
pressures were used in an attempt to enlarge the role of sputter etch-
ing in the process. The IV characteristics of junction obtained in
these runs exhibited large (subgap) leakage currents. This is in
general agreement with results obtained with the rf plasma method (15).
These conclusions are only tentative, however, and experiments have

been planned to pursue these studies in a better vacuum system, in which background gases can be better controlled.

The system parameters which determine the final oxide thickness include, among others, oxygen pressure, beam current density, and oxidation time. Other possible influential variables, such as accelerator and discharge voltages and argon pressure, were held constant in these experiments. The behavior of oxide thickness (as determined by junction resistance or current density), as a function of changes in these parameters, was observed to be reproducible, but did not show any simple form. Increases in oxygen pressure, beam current density, and oxidation time all brought about significant changes in final oxide thickness, but oxide thickness was not in simple proportion to ion dose.

There are two sources of oxygen which contribute to the growth of the oxide film: positive oxygen ions from the beam and neutral gas which is not ionized in the discharge chamber. The film will adsorb neutral oxygen (the time necessary to adsorb a monolayer is of order $10^{-2}$ sec at a pressure of $10^{-4}$ torr), and the ion beam supplies energy which can help react adsorbed oxygen. In addition, the ion beam can cause ionization of neutral gas atoms. In order to grow an oxide film, the oxygen must be transported through the growing film to the metal-oxide interface. The energy supplied by the beam can also affect this process.

Estimates of the contribution of the oxygen ions in the beam to the oxide growth reveal that it is an important factor, but that there are insufficient ions present in the beam to account for the total oxide thickness. Adsorbed neutral oxygen, reacting with the aid of energy supplied by the beam would explain the difference. Experiments are being considered which would use an ion mill system in which a larger ratio of pressure in the ion mill discharge chamber to bell jar pressure could be maintained. This would result in a smaller neutral oxygen concentration in the substrate region, enhancing the effect of the beam, and allowing greater control of the process.

The ion beam contains both argon and oxygen. It is difficult to even guess at the proportions. Negative oxygen ions play a prominent role in argon-oxygen discharges (15), and are believed to be important in rf plasma oxidation (3), but they are not extracted by the grids of the ion mill. Heats of formation of positive oxygen ions ($O^+$, $O_2^+$) are similar to that of argon ions, but larger than those of negative oxygen ions ($O^-$, $O_2^-$) (15). The use of a mass spectrometer to probe the makeup of the beam would help to clarify the situation. The use of a pure oxygen beam would remove the complicating effects of the argon ions, but would also speed up oxidation. With niobium, the argon is needed at least as a dilutant (3,15) because niobium tends to oxidize rather easily.

In principle, thermal oxidation involving the neutral oxygen

could play a role in the oxide growth. The influence of thermal oxidation, unaided by the ion beam, was investigated by fabricating junctions using oxygen at pressures typical to ion milling, but without the ion beam. The resulting current-voltage characteristics showed critical currents well in excess of $10^6$ amp/cm$^2$ with no features associated with tunneling. Therefore, we conclude that thermal oxidation plays no significant role in the process.

## IV. JUNCTION PROPERTIES

The principal aim of this work was the construction of small, high current density niobium Josephson devices. The motivation behind this was the fact that the hysteresis parameter $\beta$ (23) is inversely proportional to critical current density. For most applications, a low $\beta$ (non-hysteretic IV) is desirable. We felt it important to investigate the limits of high current density for niobium oxide barrier junctions. We have attained critical current densities as high as $6.5 \times 10^5$ amp/cm$^2$. For such a junction, the calculated value of $\beta$ is approximately 0.2, while the observed ratio of lower switching current to critical current was .61. Experiments are in progress to investigate still higher critical current densities, the effect of the non-equilibrium state induced by extremely high quasiparticle injection, and the usefulness of external resistive shunting to remove hysteresis completely in these junctions.

Junctions with moderate critical current densities (below about $10^4$ amp/cm$^2$) were characterized by very small currents at voltages below the sum of the energy gaps. A typical current-voltage characteristic is shown in Figure 3. From the structure at the difference of the energy gaps and the steep rise at the gap sum, it was determined that $\Delta_{Nb}$ and $\Delta_{Pb-Bi}$ were 1.5 and 1.7 meV, respectively, in agreement with accepted values. (Note: All reported measurements were taken at 4.2K. Nb and Pb alloy transition temperatures were 9.2 and 8.4 K.) Using these values, the product of critical current ($I_C$) and normal state resistance ($R_N$, taken to be the dynamic resistance for voltages well above the gap) is predicted to be 2.5 mV at T=0 (24). Typical observed $I_C R_N$ products were in the range 1.5-1.8 mV. The product $\Delta I \, R_N$, where $\Delta I$ is the size of the step at the sum of the energy gaps, was typically 2.5 mV. The quasiparticle current at subgap voltages, when fitted to a straight line, yields a characteristic resistance $R_J$. Ratios $R_J/R_N$ larger than 20 and products $I_C R_J$ as high as 30 mV were obtained with junctions having critical current densities of $10^3$ amp/cm$^2$.

For junctions with critical current densities approaching or exceeding $10^4$ amp/cm$^2$, the hysteresis in the current-voltage characteristic was reduced as critical current density increased. The current-voltage characteristic for such a junction is shown in Figure 4. The hysteresis parameter (23), from the resistively shunted junction model, provides an indication of the degree of hysteresis expected. Realiz-

ing that $I_C R_N$ is a characteristic of the materials used, we express $\beta$
as:

$$\beta = \frac{2\pi}{\phi_o} (I_C R)^2 \left(\frac{\varepsilon \varepsilon_o}{J_C w}\right),$$

where $J_C$ is the critical current density, w is the oxide thickness and
$\varepsilon$ is the relative dielective constant of the oxide. (Since capaci-
tance increases linearly as oxide thickness decreases, while critical
current increases exponentially, $\beta$ is decreased by going to high cur-
rent densities.) Using values of $\varepsilon$ and w extrapolated from work on
junctions fabricated using the rf plasma method (25), we obtained
values of $\beta$, for junctions having critical current densities of $10^4$
and $10^5$ amp/cm$^2$, of 9.2 and 1.0. Comparison of experimental data with
model calculations which include the nonlinear quasiparticle charac-
teristic (26) yielded satisfactory results.

Results for thermally cycled junctions (room temperature to 4K
and back to room temperature) were quite satisfactory. Some of the
junctions were cycled up to eight times over a period of weeks with
only very small changes in resistance and essentially no qualitative
change in quasiparticle characteristic. Extensive cycling and life-
time tests have not been performed, however, good thermal cyclability
of Nb/Pb junctions has been noted by other workers (27), and the
superior properties of the $\varepsilon$ phase of Pb-Bi (as compared to other Pb
alloys) have recently been reported (19).

Although our experimental set-up was not conducive to study of
the uniformity of the process (i.e., variation from run-to-run in
critical current density or other junction properties), some relevant
comments can be made: Critical current densities of 8 samples on a
single substrate typically varied by a factor of 2-3, and the factor
could be made smaller than 1.5 if the sample was well aligned in the
ion beam. Variations in critical current density in samples fabri-
cated in different runs were usually larger, but the variation could
be kept within a factor of 3 if care was taken. (Note that a mono-
layer of oxide corresponds to roughly an order of magnitude change in
critical current density.) Improvement in uniformity should be possi-
ble through use of a large diameter and very uniform ion beam, and a
system in which the ion mill position was well fixed relative to the
substrate table (our ion mill was removable and its position on the
base plate of the vacuum system was not well fixed). Also, substrate
rotation would help uniformity. Finally, care must be taken in align-
ing the ion beam current density probe with respect to the beam and
substrate.

Incidentally, the edge junctions tended to be more uniform in
properties than the simple overlap junctions. This is due to the fact
that the growth of oxide was faster on the top film surface than on
the edge of a film. Since the edge can contribute significantly to
the properties of a small overlap junction, this can introduce a vari-
ability into the overlap junctions which is not well controlled.

## SUMMARY

We have successfully applied a new oxidation technique to the fabrication of very small, very high current density niobium-based tunnel junctions. The technique utilizes the advantages of ion beams in growing oxide tunneling barriers, and is quite flexible, putting no special requirements on system vacuum or preparation.

The motivation for this work has been the study of Josephson junctions and, although the contributions of various mechanisms to the growth of the oxide are not well understood at the present time, the technique has yielded Josephson junctions of excellent quality and has led to the reproducible fabrication of submicron devices with unsurpassed critical current densities.

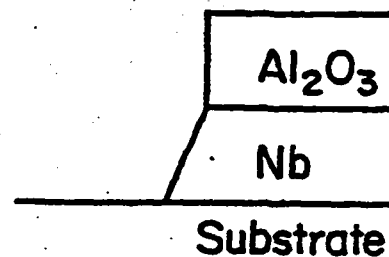## ACKNOWLEDGMENT

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Figure 1.   Formation of edge by ion milling (schematic).
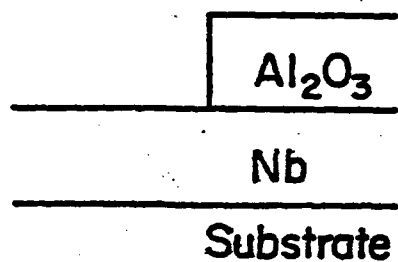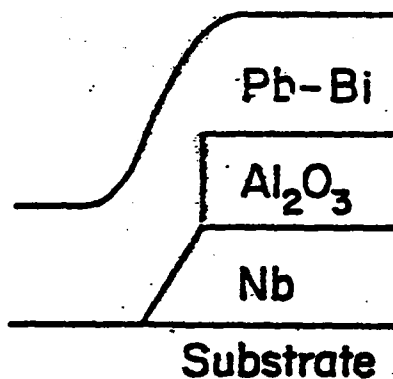


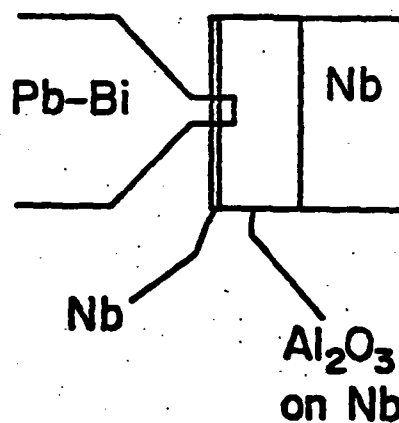(a)   Before milling (Ar beam).          (b)   After milling.

Figure 2.   Josephson junction with edge geometry (schematic).
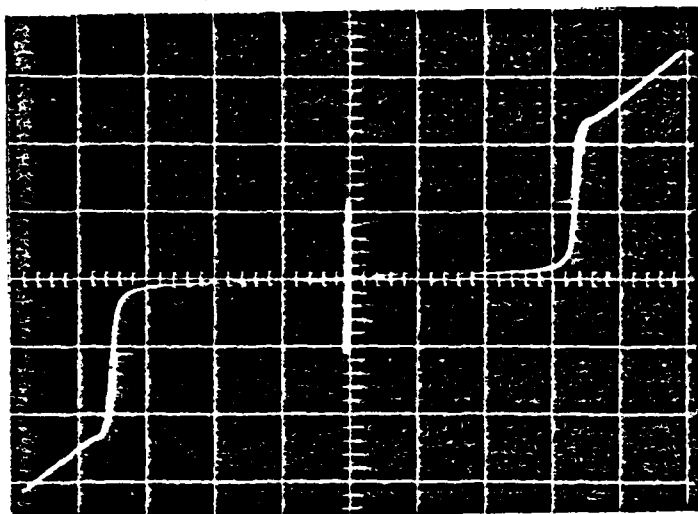


(a)   End-on view.          (b)   Top view.

Figure 3.   Current-voltage characteristic of a junction having a
critical current density of 1.3 x $10^3$ amp/cm$^2$.   Scales are 0.5 mA and
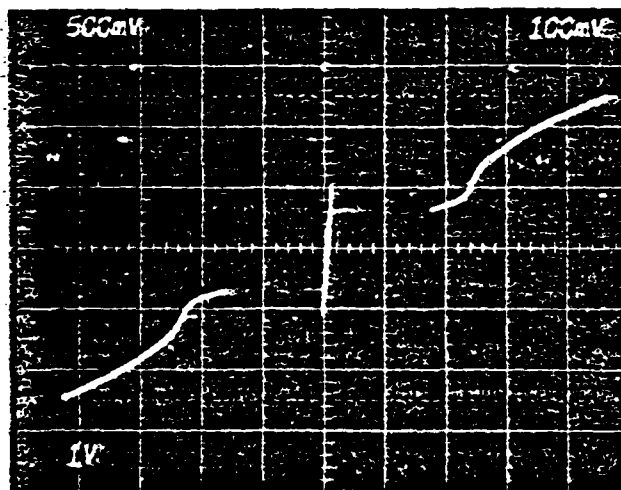1 mV per division.



Figure 4.   Current-voltage characteristic of a junction having a
critical current density of 2.6 x $10^5$ amp/cm$^2$.   Scales are 0.5 mA and
1 mV per division.